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B.N. Brogdon, D.R. Dimmel, and T.J. McDonough

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PHYSICO-CHEMICAL PROCESSES LIMITING LIGNIN REMOVAL DURING BLEACHING EXTRACTION

Brian N. Brogdon
Ph.D. Candidate

Donald R. Dimmel
Professor of Chemistry

Thomas J. McDonough
Professor of Engineering

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, GA 30318-5794
USA

ABSTRACT

Delignification of chlorine dioxide treated pulps with an acid ethanol extraction stage (A_E) was less effective than an aqueous caustic extraction stage (E). Calculated effective lignin diffusion coefficients (***D***) from A_E-stages were generally much lower than those for an aqueous E-stage. The slow lignin removal process of the A_E-stage was analogous to aqueous lignin leaching of unbleached pulps. These two extraction processes seemed to have similar diffusion limiting mechanisms, namely lignin association within the fiber wall. The difference in delignification efficiency of an A_E-stage versus an aqueous E-stage is presumably related to how each process disrupts the associated lignin complex. An aqueous E-stage, unlike the A_E-stage, can breakup associated complexes by the electrostatic repulsion of ionized acid groups.

Keywords: Acid, activation energy, alcohols, alkaline, association, bleaching, chlorine dioxide, delignification, diffusion, ethanol, extraction, kraft pulps, leaching, lignin, organosolv, pore size, solubility, swelling.

INTRODUCTION

Our ongoing investigations of "organosolv bleaching" have yielded some interesting data on how delignification is affected when the lignin extraction stage medium is changed from aqueous to ethanol-water solutions [1]. An earlier report has examined the effect of ethanol-water media on the E-stage of a DE partial bleaching sequence [2]. Extraction delignification was strongly inhibited when an aqueous medium was switched to an ethanol medium (Fig. 1). A subsequent study determined that the solubility of oxidized lignin in alkali was limiting delignification with ethanol-water media [3].

These results prompted us to examine an alternative extraction stage for chlorine dioxide bleached pulp, namely an acidic ethanol extraction stage (A_E-stage) [4]. Under the acidic conditions ($[H^+] \geq 10^{-5}$ M), the oxidized lignin, containing carboxylic groups, is expected to be more soluble in ethanol-water solutions than in water. This expectation is based on the solubility behavior of carboxylic acids and on the dissolution of lignin with acid organosolv pulping processes [1,3-6]. More delignification could be achieved with a 90% ethanol medium than with water under acidic conditions ($10^{-4} \leq [H^+] \leq 10^{-2}$ M). However, the A_E-stage requires high temperatures and longer reaction times to achieve the same post-extracted kappa number as an aqueous E-stage [1,4].

Recently, we have examined lignin removal in an ethanol-based DA_E partial bleaching sequence [1,7]. The results indicate that 25 to 30% of the residual lignin entering the A_E-stage can be removed (Table 1). An aqueous E-stage in a DE partial bleaching sequence, on the other hand, can remove 55% of the entering residual lignin. Again, an aqueous E-stage is more efficient at delignification than an A_E-stage.

Table 1. Residual lignin removal with aqueous- and ethanol-based partial bleaching sequences [1,7].

Treatment	Bleaching Medium	Residual Lignin (%)
Unbleached	-	4.63
D	Water	2.99
DE	Water	1.37
D	90% EtOH	3.02
DA_E	90% EtOH	2.18

These studies have indicated some significant differences in the ability of various media to extract oxidized lignin [2-4,7]. What makes an aqueous E-stage more efficient at delignification than an A_E-stage? The answer could be related to physico-chemical factors that have been proposed for an analogous extraction process, aqueous lignin leaching from unbleached pulps [8-13]. In this paper, we examine the similarities between the A_E-stage and lignin leaching, and determine what possible factors are contributing to the lower delignification efficiency of the A_E-stage.

RESULTS AND DISCUSSION

Effective Lignin Diffusion Coefficients in Various Media

Comparisons of Effective Diffusion Coefficients

Separate studies have estimated and analyzed the effective diffusion coefficients (***D***) of oxidized lignin during extraction with acidic [4] and alkaline ethanol-water [2] media. These ***D*** values are compiled in Table 2 along with the estimated ***D*** values of aqueous E-stage [2] and from other alcohol-water media, and with the reported ***D*** values for aqueous lignin leaching of unbleached pulps [9,12]. Most of the lignin extractions performed under alkaline conditions had equivalent ***D*** values, namely on the order of 10^{-11} cm^2/s. The ***D*** values for acidic or neutral conditions were similar (~10^{-13} cm^2/s) and were much lower than the ***D*** values for alkaline conditions. These comparisons suggested that the removal of dissolvable lignins from unbleached and D-stage treated pulps responded to alkalinity in a similar way, irrespective of the medium.

Enhanced Diffusion at Elevated Temperatures

Increasing the temperature of an A_E-stage to 100°C increased the ***D*** to approximately the same order of magnitude as alkaline extraction processes at 60°C (Table 3). Likewise, acid extractions performed with other alcohols exhibited an order of magnitude increase in ***D*** when the temperature was increased to 100°C. This effect was analogous to the increase in ***D*** with increased temperature to 90°C for lignin leaching of unbleached pulps (Table 3).

Table 2. Comparisons of D from different lignin extraction processes with various media.

Pulp	Ref.	Extraction Medium	Temp. (°C)	D ($cm^2/s \cdot 10^{12}$)
D-stage	[2]	Water/0.07 M NaOH	60	9.9
D-stage	[2]	75% EtOH/0.07 M NaOH	60	4.7
D-stage	[4]	90% EtOH/0.01 M HCl	55	0.41
D-stage	[1]	90% *n*-PrOH/0.01 M HCl	55	0.41
D-stage	[1]	90% *t*-BuOH/0.01 M HCl	55	0.33
Kraft	[12]	Water/0.2 M NaOH	60	8.8
Kraft	[9]	Water/near neutral pH	60	0.097

Table 3. Effect of elevated T on D for acid alcohol extractions and brownstock lignin leaching.

Pulp	Ref.	Extraction Medium	Temp. (°C)	D ($cm^2/s \cdot 10^{12}$)
D-stage	[4]	90% EtOH/0.01 M HCl	100	3.4
D-stage	[1]	90% *n*-PrOH/0.01 M HCl	100	3.7
D-stage	[1]	90% *t*-BuOH/0.01 M HCl	100	1.5
Kraft	[9]	Water/near neutral pH	90	0.47

The striking resemblance between acid alcohol extraction and aqueous leaching of unbleached pulp is better seen in the D behavior over a temperature range (Figs. 2 and 3). Both processes showed the same augmentation of diffusion occurring at temperatures ≥70°C, indicating that these processes presumably have similar limiting mechanisms. Acid ethanol extraction and lignin leaching have been characterized as being diffusion-controlled, and both processes have similar activation energies (13 to 20 kcal/mole) [4,9]. Diffusion activation energies for the other acid alcohol extractions were also low (~7 to 10 kcal/mol) [1], confirming that delignification is limited to other factors besides the alcohol medium.

Review of Limiting Processes for Aqueous Lignin Leaching

Several researchers have hypothesized various factors that could be limiting the diffusion of lignin from the fiber wall during aqueous lignin leaching of brownstocks [8-13]. These particular mechanisms are discussed and are related to our A_E-stage studies in the following sections.

Fiber Pore Size Restrictions

Favis et al. [8-11] proposed that lignin diffusion, under neutral conditions, is limited by size restrictions of the fiber pores. Lignin fragments are entrapped within the fiber wall as a consequence of their molecular diameters being approximately the same size or larger than the diameters of the fiber pores. This particular model was based on the observed correlations between the sizes of lignin fragments (estimated from molecular weight distribution data) and the sizes of fiber pores during various wood pulping processes [14]. Favis noted in one of his reports, however, that the spherical diameters of the leached lignin fragments (~10 nm), at various wash times, were generally larger than the median pore size (4 nm) [15]. This apparent inconsistency was resolved if the fragment shape was assumed to be an oblate ellipsoid [8,11,15].

Another key piece of evidence that Favis used to substantiate his pore restriction model [8,11] was the effect that electrolytes had on the lignin leaching rate [10]. The leaching rate was strongly inhibited when the ionic strength of the aqueous medium was increased with inorganic salts; this effect was intensified for divalent cations (e.g., Mg^{+2}) versus monovalent cations, (e.g., Na^{+}). In general, cations have been shown to decrease in fiber swelling by as much as 20% [16]. Favis claimed that the inhibited lignin diffusion with electrolytes was due to the reduction in fiber pore size (~4%) brought about by a 10% reduction in fiber swelling [8,11]. His previous data interpretation suggested that the average fragment size was close to the average pore size. Favis' diffusion model predicted that lignin leaching would be eliminated if the pore size decreased by 4%. This particular model, however, neglects the effect that cations have on the solubility of lignins [3,17].

Self-Association of Lignin

Another possible limiting mechanism for lignin diffusion is lignin association [12,13]. Association can affect lignin solubility or colloidal stability in a medium [17,18]. Reports of lignin association have been discussed extensively in the literature, especially in the determination of molecular weight distributions of dissolved lignins [19-24].

The major forces that can cause lignin fragments to associate with one another include hydrogen bonding and stereoregular association [19]. Hydrogen bonding forces are typically very strong (~5 kcal/mol) due to the short distance between the dipoles. This type of interaction can occur between phenolic, aliphatic hydroxyl and ether groups, or between hydroxyl groups and the π-electron systems of aromatic moieties [25]. Stereoregular association is caused by van der Waals forces arising from the HOMO-LUMO interactions of the π-orbitals between fragments. Furthermore, Sarkanen et al. [20,22] have indicated that there can be different levels, or modes, of lignin association. On the smallest level, discrete lignin fragments can associate with one another to form an ensemble. Afterwards, the ensembles can also associate with one another and form larger complexes. Evidence of such modes of association comes from the kinetics of kraft lignin association/dissociation in various media [20,25].

The association/dissociation of lignin fragments is also strongly influenced by several factors, such as alkalinity and inorganic constituent concentrations in the medium. Kraft lignins in aqueous media typically exhibit low levels of association at high pH (>13). According to Rudatin et al. [19], the majority of kraft lignin association occurs when the pH of the solution is lowered from 13 to 11; below pH 10 there was little additional association. Rudatin et al. have ascribed the pH dependency of association to the protonation of the phenoxide ions and the subsequent hydrogen bonding of phenolic groups with other electronegative elements. Studies performed by Lindström [17] have shown that multivalent cations can cause aqueous kraft lignin sols to associate with one another and precipitate out of solution. The multivalent cations can act as ionic bridges between anionic groups that would otherwise repel one another.

In alkaline leaching studies of unbleached pulps, Li et al. [13] have observed that D values increase from 10^{-15} to

10^{-9} cm^2/s, and the rates of lignin removal increase as the pH value is increased from neutral to 14. They proposed that lignin leaching is limited by the associated state of the lignin within the fiber [12,13]. Increasing the alkali concentration increases the mobility of the associated lignin by causing the associated complex to breakup into smaller and smaller ensembles. The smaller ensembles can more easily diffuse out of the fiber wall than the larger associated complex. Li et al. [12,13] have examined the effect of fiber swelling and various electrolytes on alkaline leaching. However, their results indicated no correlations between the reduction of lignin diffusion and the reduction in pore size that was caused by electrolytes.

Lignin Association with Cellulose

The association of lignin fragments with cellulose (i.e., lignin adsorption onto cellulose) could also limit lignin diffusion during extraction. This particular limiting mechanism has been considered as a minor factor by Li and MacLeod [12]. Lignin fragments could associate with cellulose through hydrogen bonding of the cellulose hydroxyl groups with the electronegative elements or the π-electron systems of lignin [25]. Evidence of this type of lignin-cellulose association in the literature is sketchy at best. An analogous system is the association (adsorption) of aromatic dyes by cellulose substrates; however, most of the textile literature suggests weak interactions between aromatic dyes and cellulose hydroxyl groups in aqueous solutions [26].

Severtson [27] has examined the sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol onto softwood kraft fibers in aqueous solutions. His results indicated that pH and lignin concentration of the fiber substrate strongly affected chlorophenolate adsorption; it is low at >7 pH and high at <6 pH. This effect was attributed to the ionization of the chlorophenols (pK_a ~7-8). The chlorophenols adsorbed very strongly onto high lignin content fibers (kappa 105) as opposed to negligible adsorption onto cotton linters (kappa ~0). Similar behavior has also been reported with the adsorption of aromatic compounds onto low and high lignin pulps [28,29].

Limiting Processes for the Acid Ethanol Extraction Stage

A number of limiting factors have been hypothesized for lignin diffusion from unbleached pulp fibers in water. Each of the factors was analyzed to see if any applied to our observations with A_E-stage treatment of D-stage treated pulps.

Favis' pore restriction model was eliminated as a factor based on some of our earlier caustic extraction results in ethanol-water solutions [2]. The sizes of the extracted lignin fragments (<1.4 nm) were generally smaller than the average size of the fiber pores (4-6 nm). The observed decreases in fiber swelling in ethanol-water solutions, ~12%, would roughly decrease the average pore size by ~4%. This small reduction in pore size with ethanol-water solutions was determined to contribute negligibly to lignin diffusion resistance. In addition, there was no correlation between decreased fiber swelling and decreased $\boldsymbol{D}$, even in other aqueous de-swelling media [2]. The same basic argument can be made for the A_E-stage. The sizes of the lignin fragments will presumably be similar to those observed in aqueous D- or E-stage effluents (1-3 nm) [1,2], and the slight reduction in pore size from fiber de-swelling should not contribute significantly to diffusion resistance. Actual measurement of the molecular weights and sizes of the A_E-stage dissolved lignins would be needed to further substantiate this assumption.

Oxidized lignin association with cellulose (i.e., lignin absorption directly onto cellulose) was also eliminated as a major limiting mechanism in diffusion resistance with the A_E-stage. Evidence from the literature suggests that the association interactions among cellulose hydroxyl groups and aromatic moieties are very weak, and that the absorption of aromatic molecules onto fibers is strongly dependent upon the residual lignin contained within the fiber [27]. It is likely that the hydroxyl groups on the cellulose are strongly hydrogen bonded with water or ethanol molecules in the media [26]. This tightly held layer of solvent molecules will be difficult for a lignin fragment to displace and associate directly with the cellulose substrate. It is more probable that lignin association with cellulose is indirect and occurs through association with lignin that is chemically bonded with the carbohydrates.

The association of oxidized lignin appears to be the major limitation in lignin diffusion with the A_E-stage. Current lignin leaching studies with unbleached pulps strongly indicate that lignin association is limiting its removal from the fiber wall in aqueous media [12,13]. Various degrees of lignin association in non-aqueous and organic solvent-water solutions have been documented in the literature [21-24]. Furthermore, the oxidized lignin of D-stage pulp contains a higher concentration of carboxylic acid and other oxygen containing groups than the original kraft lignin. This will increase the number of hydrogen bonding sites on the lignin fragments and possibly increase the probability of lignin association. Berry [30] and Jokela and Salkinoja-Salonen [31] have cited possible evidence of oxidized lignin association with isolated extraction lignins.

In addition, the observed $\boldsymbol{D}$ enhancement at higher temperatures ($\geq$ 70°C) could be another indication of lignin association for the A_E-stage (Fig. 2). A previous study [4] suggested that this sudden increase in $\boldsymbol{D}$ was related to the decreased hydrogen bonding of medium as the temperature approached the boiling point. This particular mechanism was proposed by Johansson [32] to explain the enhanced $\boldsymbol{D}$ for brownstock leaching in water (Fig. 3). Although such a mechanism is plausible for acid alcohol extraction, one would expect the onset of this enhancement to change with each extraction medium because the boiling point of each medium is different. Instead, all the acid alcohol extractions have basically the same onset of enhanced $\boldsymbol{D}$ as the aqueous lignin leaching system (~70°C). An alternative explanation is that the increase in the extraction temperature ($\geq$70°C) is diminishing the hydrogen bonding that causes the lignin to associate into complexes. The breakup of these complexes into smaller, more mobile ensembles would presumably decrease the diffusion resistance [1].

Explanations for Oxidized Lignin Extraction Efficiencies

Lignin association may also explain why an A_E-stage is less efficient than an aqueous E-stage. The alkali in an aqueous E-stage ionizes the carboxylic groups in the oxi-

dized lignin; these ionized groups repel one another and disrupt the associated lignin complexes into smaller fragments. Li et al. [12,13] have cited this electrostatic repulsion mechanism for the effectiveness of brownstock lignin leaching under alkaline conditions. Such a lignin dispersing mechanism will not occur under the acidic conditions of an A_E-stage; the acid groups on the lignin will not be ionized to a significant extent.

Our previous studies have indicated the ineffectiveness of caustic extraction performed with ethanol-water media due to solubility problems [2,3]. This factor can also be rationalized in terms of lignin association and solvation effects. Ethanol is not as good as water at stabilizing separated ion pairs; the bulky alkyl group of ethanol interferes with the ion-dipole interactions that stabilize charge-separated ions in solution. It is likely that the ionized carboxylic anions (ROO^-) and Na^+ exist as an intimate, non-solvated ion pair (ROO^-Na^+) in ethanol-water solutions [1]. Thus, the lignin remains as an associated complex with the electrostatic repulsive ROO^- groups effectively shielded by Na^+.

CONCLUSIONS

Lignin removal from a D-stage treated pulp is less efficient in an A_E-stage than an aqueous E-stage. The strong similarities between acid ethanol extraction and aqueous brownstock lignin leaching suggest that both lignin diffusion processes are limited by a common mechanism. Several researchers have hypothesized that lignin removal during brownstock leaching is restricted by the association of lignin inside the fiber wall. Improvements in aqueous lignin diffusion with higher alkali concentrations appear to be related to the disruption of lignin complexes by the electrostatic repulsion of ionized groups. A similar type of mechanism probably occurs in an aqueous E-stage. The acid conditions of the A_E-stage, however, do not promote the dissolution of associated lignin by an electrostatic repulsion mechanism. In addition, ethanol-water solutions are less effective at stabilizing ion pairs than water. Consequently, E-stages performed in ethanol-water solutions will be less effective due to the shielding of ionized acid groups by the corresponding counterions.

EXPERIMENTAL PROCEDURES

A thoroughly washed conventional softwood kraft pulp (southern pine) was obtained from a mill and had a kappa number ~30. The specific conditions of the D-stage, A_E-stage, and E-stage have been previously reported [1-4,7].

Acid alcohol extractions (*n*-PrOH and *t*-BuOH) were performed on 2.5 o.d. gram samples of the aqueous D-stage treated pulp that had a kappa of 18.8. Experiments were conducted at 1.25% consistency in 90% ethanol medium with 0.01 M HCl. Low temperature reactions (≤70°C) were conducted in sealed containers, which were heated using a water bath. High temperature reactions (≥70°C) were performed in a 300-mL Teflon-lined Parr bomb reactor heated by an oil bath. Generally, the high temperature reactions (100°C) required 10 minutes to heat up to the specified reaction temperature. The pulps were extracted for the required period, cooled to 65 to 70°C (if needed), and drained of extraction effluent to ~25% consistency.

The estimation of D from the experimental data has been previously explained [1,2,4].

NOMENCLATURE

A_E	acid ethanol extraction stage
D	chlorine dioxide stage
D	effective diffusion coefficient, (cm^2/s)
D_T/D_{20}	relative diffusion coefficient, ratio of D at some T to D at 20°C
E	caustic extraction stage
T	reaction temperature, (°C)

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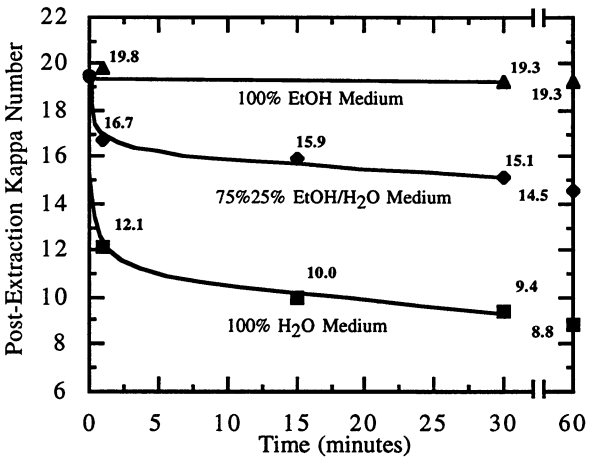

Figure 1. Low consistency (0.5%) alkaline extraction of a 19.5 kappa D-stage treated pulp with aqueous and ethanol-water solutions [2].

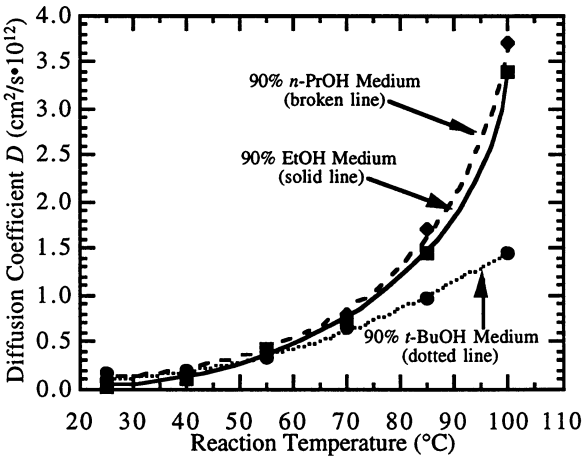

Figure 2. Calculated effective diffusion coefficients for lignin (***D***) for various acid alcohol extractions at t=5 hrs.

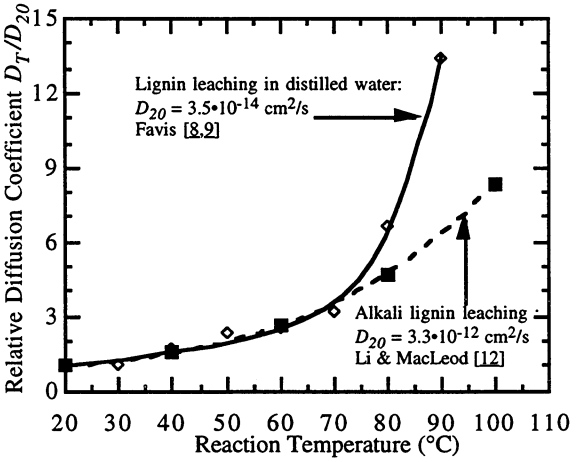

Figure 3. Relative effective diffusion coefficients for lignin during leaching under neutral and alkaline conditions with softwood kraft pulps [8,9,12].